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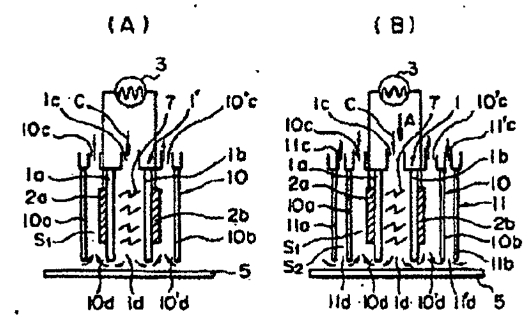
(54) [Title of the Invention] ATMOSPHERIC PLASMA SURFACE TREATMENT DEVICE

(57) [Abstract]
[Object] To provide an air blow-off type of plasma surface treatment device that is capable of either preventing the remaining part of the reactive gas and the by-products from becoming diffused into the surrounding area after the treatment process is completed or at least decreasing the amount of the diffusion.
[Constitution] It is a constitution that provides a box frame 10 to form a space for suctioning the blow-off gas and that is disposed onto the outer periphery of a reaction container 1 consisting of a dielectric having electrodes 2a and 2b and further provides an exterior box frame 11 that forms another space in the outer circumference thereof so that inert gas does not infiltrate into the atmospheric reaction container when it is introduced into the device. In addition, a device as a separate embodiment is a constitution that provides a receptacle box disposed onto the opposite side of the reaction container in relation to the object to be treated for when the object to be treated is fibrous, wherein said receptacle box has a slightly larger opening than the opening for blowing out the inert gas from the exterior box frame and the gas following completion of the treatment process.



1a,1b: 側壁
1c: 導入口
1d: 吹出し口
2a,2b: 電極
3: 電源
10: 箱体
10a,10b: 側壁
10c,10'c: 吐き出し口
10d,10'd: 吸引口
11: 外箱体
11c,11'c: 導入口

1a, 1b: side walls
1c: inlet
1d: outlet
2a, 2b: electrodes
3: power source
10: box frame
10a, 10b: side walls
10c, 10'c: outlets
10d, 10'd: suction inlets
11: exterior box frame
11c, 11'c: inlets

[Claims]

[Claim 1] An atmospheric plasma surface treatment device in which a mixture of gases consisting of a reactive gas, such as a fluorocarbon gas or a hydrocarbon material, and an inert gas, consisting of a noble gas such as helium, argon, neon or N_2, are introduced at atmospheric pressure into the device from one end of a space between a pair of electrodes disposed so as to face each other, said mixture of gases is blown across the surface of the object being treated that is placed either in a stationary or mobile orientation between the pair of electrodes at the other end, and is plasma-enhanced under high frequency and high voltage by means of an electric glow discharge so as to reform the surface of the object being treated or form an amorphous carbon film on the surface by means of deposition formation;

wherein said surface treatment device comprises a box-shaped or cylindrical dielectric reaction container having opposing side walls disposed in parallel to one another so as to maintain a prescribed distance from one another, a pair of side walls disposed at a prescribed distance from one another between the surface of the object being treated and the aforementioned pair of electrodes, both of which are disposed onto the outer surface of the aforementioned opposing walls, a peripheral wall connecting the front and rear ends of the aforementioned side walls, and a top wall that covers the upper surface of the side walls and the peripheral wall, in which the inlet for introducing the aforementioned mixture of gases located at the center of the top wall is opened and the space between the lower ends of the aforementioned side walls and the object being treated forms an outlet for blowing out the gas following completion of the treatment process;

wherein said atmospheric plasma surface treatment device is characterized as having a pair of side walls that enclose the reaction container and that form a space between themselves and the surface of both electrodes disposed on the outer periphery, a peripheral wall connecting the front and rear ends of the aforementioned side walls and a top wall that covers the upper surface of the side walls and the peripheral wall, a pair of outlets for blowing out the gas following completion of the treatment process that are disposed above the top wall to be nearly symmetrical in relation to the inlets for introducing the mixture of gases in the reaction container and a dielectric box frame that is disposed so a prescribed distance is maintained by the lower end of the side walls in relation to the object being treated and in relation to the lower end of the reaction container, so that the gas that is blown out following completion of the treatment process from the lower end of the reaction container flows in an upward direction into the space between the side walls of the box frame and the side walls of the reaction container, is passed through the outlets, and is then recovered.

[Claim 2] An atmospheric plasma surface treatment device, characterized in that the atmospheric plasma surface treatment device as described in Claim 1 comprises another dielectric exterior box frame additionally provided on the outer periphery of the aforementioned box frame, wherein this exterior box frame encloses the aforementioned box frame and further comprises a pair of opposing walls that are disposed onto the outer periphery to form a prescribed space between themselves and the exterior surfaces of both side surfaces of the aforementioned box frame, a peripheral wall connecting the front and rear ends of the aforementioned side walls, a top wall that covers the upper surface of the side walls and the peripheral wall and a pair of inlets for introducing the inert gas that are opened in a nearly symmetrical position on the exterior sides of a pair of outlets for blowing out the gas following completion of the treatment process that are disposed above the top wall, such that the lower ends of the aforementioned side walls are disposed so as to maintain a prescribed distance in relation to the object being treated, the inert

gas flows through the space between the exterior surfaces of the side walls of the box frame and the interior surfaces of the exterior box frame, flows into the space between the side walls of the box frame and the side walls of the reaction container, is blown out to prevent external air from entering the reaction container, then flows into the box frame together with the gas from after completion of the treatment process, passes through the outlets located above the top wall and is recovered.

[Claim 3] An atmospheric plasma surface treatment device, characterized in that for the atmospheric plasma surface treatment device as described in Claims 1 or 2, the aforementioned object to be treated is treated as it is moved from one of the aforementioned electrodes toward the other electrode, the lower ends of both pairs of side walls of the reaction container and the box frame are inclined inward toward the vertical center axis of the pair of electrodes, and the lower ends of the pair of side walls of the exterior box frame are inclined outward in relation to the aforementioned vertical center axis.

[Claim 4] An atmospheric plasma surface treatment device in which a mixture of gases consisting of a reactive gas such as a fluorocarbon gas or a hydrocarbon material and an inert gas consisting of a noble gas such as helium, argon, neon or N_2 are introduced at atmospheric pressure into the device from one end of a space between a pair of electrodes disposed so as to face one another, said mixture of gases is blown across the surface of the object to be treated that is placed either in a stationary or mobile orientation between the pair of electrodes at the other end, and is plasma-enhanced under high frequency and high voltage by means of an electric glow discharge so as to reform the surface of the object to be treated or form an amorphous carbon film on the surface by means of deposition formation;

wherein said object to be treated is either a woven or knitted permeable fibrous material through which the aforementioned mixture of gases is able to pass, and

wherein said surface treatment device comprises a box-shaped or cylindrical dielectric reaction container having opposing side walls that are disposed parallel to one another so as to maintain a prescribed distance from one another and so as to maintain a space consisting of a prescribed distance between the upper side of the object to be treated and the aforementioned pair of electrodes, which are both disposed on the outer surface of the aforementioned opposing walls, a peripheral wall connecting the front and rear ends of the aforementioned side walls and a top wall that covers the upper surface of the side walls and the peripheral wall, in which the inlet for introducing the aforementioned mixture of gases located at the center of the top wall is opened and an outlet for blowing out the gas that is emitted after the treatment process is formed on the lower ends of the side walls;

wherein said atmospheric plasma surface treatment device is characterized as comprising a dielectric box frame having a pair of side walls that enclose the reaction container and that form a space between themselves and the surface of both electrodes disposed on the outer periphery in addition to forming a pair of outlets for blowing out the inert gas between themselves and the lower ends of both side walls of the reaction container, a peripheral wall connecting the front and rear ends of the aforementioned side walls, a top wall that covers the upper surface of the side walls and the peripheral wall and a pair of opened inlets for introducing the inert gas that are disposed above the top wall to be nearly symmetrical in relation to the inlets for introducing the mixture of gases in the reaction container,

and a dielectric receptacle box provided on the opposite side of the reaction container and box frame in relation to the object to be treated that has suction inlets which are opened and facing upward and which have total surface areas that are slightly larger than the gas blow-out outlets

on the reaction container and box frame, and that has blow-out outlets on its base cross section of which is an oblate quadrangle;

wherein the gas that is emitted from the reaction container after the treatment process is completed is surrounded by the inert gas that flows from the box frame to the outside of said container to form a sealed state before passing through the object to be treated, is suctioned in by the receptacle box and is then recovered.

[Claim 5] An atmospheric plasma surface treatment device, characterized in that the aforementioned object to be treated is treated as it is moved from one of the aforementioned electrodes toward the other electrode, the lower ends of the side walls of the reaction container are inclined inward toward the vertical center axis of the pair of electrodes, and the lower ends of the pair of side walls of the box frame are inclined outward in relation to the aforementioned vertical center axis and the side walls of the receptacle box are wider than the pair of side walls of the box frame and are inclined upward.

[Detailed Explanation of the Invention]

[0001]

[Industrial Field of Application] The present invention relates to a surface treating method or a thin-film formation method and device thereof, and in particular relates to a plasma surface treating method or a film formation method by atmospheric-pressure glow discharge plasma.

[0002]

[Prior Art] In the past, in order to form a carbon film or a fluorocarbon film on the surface of a solid material such as metal or ceramic material, a mixture of gases consisting of a reactive gas such as a fluorocarbon gas or a hydrocarbon material and an inert gas consisting of a noble gas such as helium, argon, neon, or N_2 was plasma-enhanced in a vacuum chamber under a high frequency electric field and treated with a coating or deposited with a thin film. However, in recent years, due to the increasing popularity of the atmospheric plasma surface treatment method and a thin-film formation method in which a vacuum generator or vacuum container are not required, developments relating to such technology have advanced and such technological information has been disclosed. Some representative examples are Patent Application No. S63-166599 (Unexamined Patent Application Publication No. H02-015171), Patent Application No. S61-193934 (Unexamined Patent Application Publication No. S63-050478) and Patent Application No. S63-138630 (Unexamined Patent Application Publication No. H01-306569). FIG. 7 is a diagrammatic elevational view of the thin-film deposition device used in the inventions cited above, and cross sectional diagram A-A of FIG. 7 is shown in FIG. 8. The structure of this device comprises a reaction container 1, which is a dielectric quadrangular box shape (or cylindrical shape) and electrodes 2a and 2b attached to the exterior surfaces of side walls 1a and 1b, which are either above and below or to the right and left of said container (left and right side walls in FIG. 8), and a mixture of gases consisting of inert gas made up of a noble gas such as helium (He), neon (Ne), argon (Ar) or N_2 and a reactive gas or a CF_4 gas such as a fluorocarbon gas or a hydrocarbon material introduced from inlet 1c of reaction container 1 that is connected to high-frequency/high-voltage power source 3 so that it flows in the direction of arrow C and the object to be treated 5 is positioned underneath outlet 1d that is on the opposite side of inlet 1c so that it moves in the direction indicated by arrow B. In such a structure, once the mixture of gases is made to flow and a high-frequency high voltage is applied to electrodes 2a and 2b, the mixture of gases is plasma-enhanced by glow discharge 7, flows in the direction of arrow D, the radical generated at this point is blown out from outlet 1d, and the surface of the object to be treated 5 is reformed or treated by means of thin-film deposition.

[0003]
[Problems the Invention is to Solve] The gas that is blown out from the aforementioned outlet not only treats the surface of the object to be treated but is also dispersed into the atmosphere, and solid and gaseous by-products are generated due to the reaction of this dispersed gas on the surface of said object, resulting in pollution of the atmosphere, which has the potential to be harmful. Therefore, it became desirable to either prevent the gas that was blown out and the by-products (solids and gases) from becoming dispersed into the atmosphere, or at the very least to reduce the amount of dispersion. It is an object of the present invention to provide a device that is capable of meeting these demands.
[0004]
[Means for solving the Problems] The present invention solves these problems by the following means.
(1) It makes use of a construction in which a box frame is provided for forming a space that suctions in the gas that is omitted after the mixture of gases that is present at the periphery of the dielectric box-shaped reaction container equipped with the electrodes is blown out of the outlets and comes into contact with the surface of the object to be treated and the treatment process is completed, and another exterior box frame is also provided that forms another space at the exterior periphery of the aforementioned box frame wherein an inert gas such as Ar or N_2 is introduced from the top of said box frame and is blow out from its lower ends towards the object to be treated. In addition, the front ends of the box frame that face the object to be treated at the side walls of the reaction container and box frame are inclined toward the vertical center axis.
(2) It consists of a construction in which a box frame is provided that defines the space in which an inert gas such as Ar or N_2 that is present at the periphery of the dielectric box-shaped reaction container equipped with the electrodes is blown out toward the object to be treated when said object is a woven fibrous substance that is permeable and a receptacle box is provided on the opposite side of the reaction container in relation to the object to be treated that defines another space for suctioning in gas that has an opening with a slightly larger area than the total area of the outlets for the mixture of gases that has already reacted and the inert gas. It consists of a construction based on Para. (1) when the object to be treated is moved during the treatment process.
[0005]
[Operation of the Invention] In the case of (1) above, the reactive gas that is introduced from the inlet is plasma-enhanced, the object to be treated is treated, at which point the gas which consists of nonreactive gas and gas by-product is suctioned into the space that is outside the reaction container and then recovered by an external recovery device. However, when the gas is suctioned in and substances present in the atmosphere commingle with the gas and affect the treatment process, an additional exterior box frame is provided for preventing said commingling and an inert gas such as Ar or N_2 is blown through the object to be treated. The exterior box frame may be omitted when substances present in the atmosphere become commingled but do not affect the treatment process. In addition, for applications in which the object to be treated is moved during the treatment process, commingling of the atmosphere can be alleviated by inclining the ends that face the object to be treated when it is positioned at the walls of the box frame or each of the spaces, ensuring recovery of the nonreactive gas and inert gas. In the case of (2) above, in which the object to be treated is a permeable fibrous material, the plasma that is blown through said object treats the object, the nonreactive gas and gas by-products pass through the object to be treated, are emitted out to the opposite side from the blow-out side and are suctioned into the

receptacle box, thus preventing pollution to the environment. When the object to be treated is moved during the treatment process, the effects are the same as those described in (1) above.

[0006]

[Embodiments] A longitudinal cross-sectional view of Embodiment 1 of the atmospheric plasma surface treatment device relating to the present invention is shown in FIG. 1 (B) and the arrow diagram of the portion of FIG. 1(B) indicated by the Arrow A is shown in FIG. 2. In these drawings, the same symbols are used for the same components as those for the prior art shown in FIG. 7 and 8. Electrodes 2a and 2b are provided on the exterior surface of side walls 1a and 1b, respectively, (shown on the left and right of the drawing) of the square dielectric box-shaped reaction container 1 shown in the plane view, and these electrodes 2a and 2b are connected to a high frequency, high voltage power source 3. A box-shaped reaction container 1 consists of the aforementioned side walls 1a and 1b, peripheral wall 1f, which is located at the front and rear of the side walls and which connects the sides shown on the right and left side of the drawing, and top wall 1e, which covers the top surface of the pair of side walls and the peripheral wall. On top of the top wall is provided a circular hole, which comprises inlet 1c for introducing the reactive gas. The bottom surface is left open to form gas blow-out outlet 1d. The object to be treated 5 is horizontally placed below side walls 1a and 1b, which are in an upright position, at a prescribed distance from the side walls. On the outer periphery of reaction container 1 is provided dielectric square box-shaped box frame 10, which has side walls 10a and 10b so as to form space S_1. The construction of the container itself is almost identical to the construction of the reaction container, so further explanation has been omitted. Outlets 10c and 10'c are provided on the left and right side at the top end of box frame 10 on each exterior side of inlet 1c of reaction container 1. The lower ends of aforementioned side walls 10a and 10b are positioned above the top surface of the object to be treated 5 so that they are at about the same height as the lower ends of side walls 1a and 1b of reaction container 1. Suction inlets 10d and 10'd are formed between the lower ends of side walls 1a and 10 a and 1b and 10b, which are located on the same sides and have the same horizontal positional relationship. Dielectric square box frame 11 is provided on the outer periphery of box frame 10 so as to further form space S_2 on the exterior side. On the top of box frame 11 at the left and right exterior sides are provided inlets 11c and 11'c, which are positioned on the exterior sides of outlets 10c and 10'c. The lower ends of side walls 11a and 11b are positioned above the top surface of the object to be treated 5 so that they are about the same height as the lower ends of side walls 10a and 10b, and outlets 11d and 11'd are formed between side walls 10a and 11a and 10b and 11b, respectively. When outside air enters the device but does not affect the treatment process, the exterior box frame 11 shown in FIG. 1(B) may be omitted, as is the case in FIG. 1 (A), and the simplified configuration using reaction container 1 may be used.

[0007] FIG. 3 is a longitudinal cross-sectional view of Embodiment 2, which is for handling a moving object to be treated 5 (from left to right as shown by arrow B in the drawing), and in this drawing, side walls 21a and 21b of reaction container 21 and the lower ends of side walls 30a and 30b of box frame 30 are inclined inward toward the vertical center axis and the lower ends of side walls 31a and 31b of exterior box frame 31 are inclined outward away from the vertical center axis, but the remaining portions of the drawing are the same as those shown in FIG. 1, and when external air enters the device but does not affect the treatment process, the exterior box frame 11 may be omitted, as is the case in FIG. 1 (A).

[0008] Next we will explain the operation of aforementioned Embodiments 1 and 2. As shown in FIG. 1 and FIG. 2, the mixture of gases consisting of a reactive gas such as CF_4 and a noble

gas such as He that was introduced from inlet 1c of reaction container 1 is plasma-enhanced by high frequency, high voltage glow discharge 7, which was applied by electrodes 2a and 2b, and the radical that is generated is blown out from outlet 1d so as to treat the surface of the object to be treated 5 and reform it, after which, the gas becomes nonreactive gas and gas by-products and is suctioned in by suction inlets 10d and 10'd into space S_1 and then recovered from blow-out outlets 10c and 10'c by a recovery device not shown in the drawing. An inert gas such as Ar or N_2 is introduced from inlets 11c, 11'c (31c, 31'c) of exterior box frame 11, flows through space S_2 of Embodiment 2, is blown over the object to be treated 5 from outlets 11d and 11'd (31d, 31'd), and a portion of the gas is suctioned in by suction inlets 10d and 10'd (30d, 30'd), but most of the gas is blown out into the atmosphere, so infiltration of the atmosphere is intercepted so that the substances present in the atmosphere do not affect the surface treatment process. As shown in FIG. 3, when the object to be treated 5 moves in the direction indicated by arrow B, the lower ends of all the side walls are bent so as to be inclined inward toward the vertical center axis of the surface of the object to be treated 5 in order to block infiltration of the atmosphere and to further ensure recovery of the gas that is emitted after the treatment process is completed.

[0009] FIG. 4 is a longitudinal cross-sectional diagram of Embodiment 3, which is applied when the object to be treated is a permeable fibrous material such as a woven or knitted material. The portion in FIG. 4 indicated by arrow A is shown in FIG. 5. For the device relating to this embodiment, the same symbols are used for the same components as those used in FIG. 1 and FIG. 2, so explanation has only been provided for the portions that are different. The object to be treated 25 is a permeable fibrous material and the structure of box frame 10 is the same as that shown in FIG. 1 and FIG. 2, but 10f and 10'f are the inlets for introducing the gas and 10g and 10'g are the outlets for blowing out the gas. Receptacle box 12, the cross section of which is square shaped, is provided on the opposite side from the side on which the gas is blown out in relation to the object to be treated 25 and has a suction inlet 12d that is opened and facing upward, and a surface area that is slightly larger than the total surface area of the gas blow-out outlets of reaction container 1 and box frame 10. Receptacle box 12 is a dielectric that has outlet 12c at its base. When external air enters the device but does not affect the treatment process, the box frame 10 may be omitted. FIG. 6 shows Embodiment 4, which is applied when the object to be treated 25 is a fibrous material and is moved (from left to right, as indicated by arrow B in the drawing) during the treatment process, and as was the case for Embodiment 2, the lower ends of both side walls 21a and 21b of reaction container 21are inclined toward the surface of the object to be treated 25, and the lower ends of both side walls 30a and 30b of box frame 30 and both side walls 32a and 32b of receptacle box 32 located underneath the box frame are all inclined outward. However if the treatment process is not affected by infiltration of the atmosphere, box frame 10 may be omitted, as was the case in Embodiment 3.

[0010] We will explain below the operation of the aforementioned Embodiment 3. As opposed to Embodiment 1 (see FIG. 1), in the case of Embodiment 3 nonreactive gas and gas by-products pass through the permeable object to be treated 25, so they are suctioned in by receptacle box 12 located on the opposite side from the treatment device, and infiltration of the atmosphere to the portion that is being treated on the object to be treated 25 is blocked by blowing out the inert gas from outlets 10g and 10'g on box frame 10. As shown by Embodiment 4 in FIG. 6, when the object to be treated 25 is moved in the direction indicated by arrow B, the lower ends of the side walls are bent, infiltration of the atmosphere is blocked, and recovery of the gas is ensured, as was the case in Embodiment 2 (refer to FIG. 3).

[0011]

[Effect of the Invention] By providing suction space at the periphery around the plasma blow-out outlet, or by providing a receptacle box that forms a suction space on the opposite side of the blow-out outlet[s] in relation to the object to be treated for when the object being treated is a permeable fibrous material, or by inclining the ends of the reaction container, box frame, exterior box frame, and receptacle box in the appropriate direction so that they face the object to be treated, the gas by-products and nonreactive gas that are still remaining after the reaction takes place and the treatment process is completed can be prevented from being emitted into the atmosphere and causing harm to the environment, and in addition, the atmosphere can be prevented from entering the reaction container and affecting the treatment process.

[Brief Description of the Drawings]

[FIG. 1] A simplified longitudinal cross-sectional view of a embodiment of the atmospheric plasma surface treatment device pertaining to the present invention. FIG. 1 (B) in this drawing shows the standard configuration.

[FIG. 2] A plane view of the portion indicated by arrow A in FIG. 1 (B).

[FIG. 3] A longitudinal cross-sectional view of Embodiment 2, which is applied when the object being treated is moved during the treatment process.

[FIG. 4] A longitudinal cross-sectional view of Embodiment 3, which is applied when the object being treated is a fibrous material.

[FIG. 5] The view as indicated by arrow A in FIG. 4.

[FIG. 6] A longitudinal cross-sectional view of Embodiment 4, which is applied when the object being treated is a fibrous material and is moved during the treatment process.

[FIG. 7] An elevational view of a conventional atmospheric plasma surface treatment device.

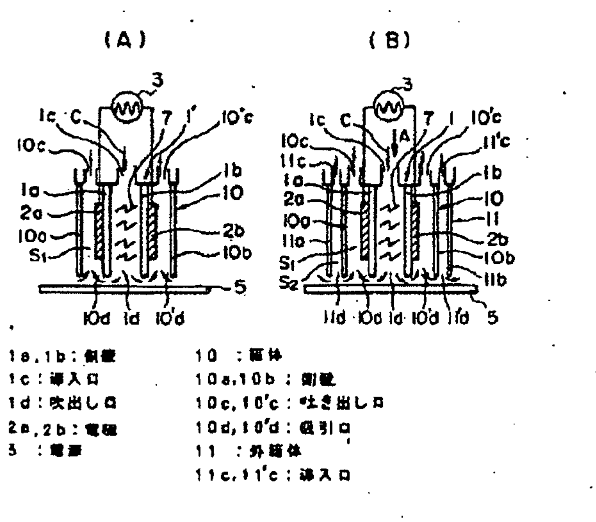
[FIG. 8] An A-A cross sectional diagram from FIG. 7.

[Explanation of Symbols]

1, 21	Reaction containers
1a, 1b, 21a, 21b	Side walls of reaction container
1c	Inlet
1d	Outlet
1e, 10e, 11c	Top walls
1f, 11f	Peripheral walls
2a, 2b	Electrodes
3	Power source
5, 25	Object to be treated
7	Glow discharge
10, 30	Box frame
10a, 10b	Box frame side walls
10c, 10'c	Box frame outlets
10d 10'd	Box frame suction inlets
10f, 10'f	Box frame inlets
10g, 10'g	Box frame outlets
11, 31	Exterior box frame
11a, 11b, 31a, 31b	Exterior box frame side walls
11c, 11'c, 31c, 31'c	exterior box frame inlets
11d, 11'd	exterior box frame outlets
12, 32	Receptacle boxes

12a, 12b, 32a, 32b	Receptacle box side walls
12c	Receptacle box outlet
12d	Receptacle box suction inlet
B, C	Arrows
S_1, S_2	Spaces

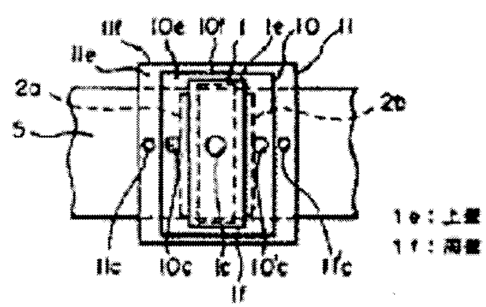
[FIG. 1]



1d: outlet
2a, 2b: electrodes
3: power sour

10: box frame
10a, 10b: side walls
10c, 10'c: outlets
10d, 10'd: suction inlets
11: exterior box frame
11c, 11'c: inlets

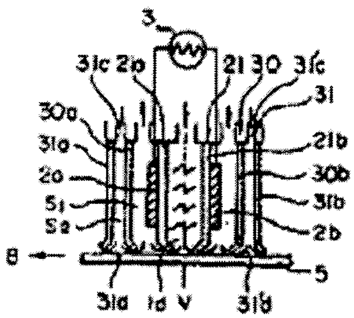
[FIG. 2]



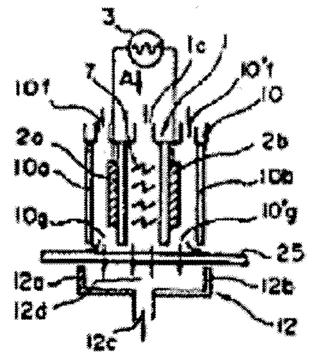
Key:
1e: Top wall

1f: Peripheral wall

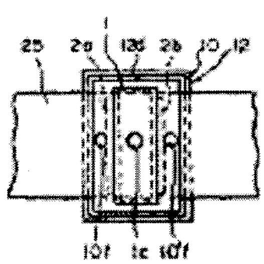
[FIG. 3]



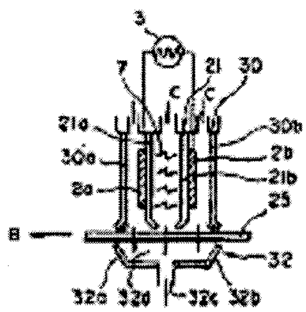
[FIG. 4]



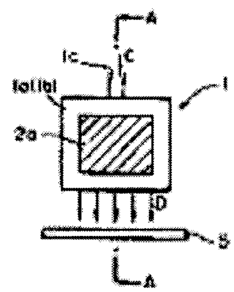
[FIG. 5]



[FIG. 6]



[FIG. 7]



[FIG. 8]